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Effects of hydroprocessing on structure and properties of base oils using NMR

Brajendra K. Sharma^{a,b,*}, Atanu Adhvaryu^{a,b}, Joseph M. Perez^a, Sevim Z. Erhan^{b,*}

^aDepartment of Chemical Engineering, Pennsylvania State University, University Park, PA 16802, USA

^bUSDA/NCAUR/ARS, Food and Industrial Oil Research, 1815 N. University Street, Peoria IL 61604, USA

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ABSTRACT

The hydroprocessing technologies such as hydrocracking, hydrofinishing provide an opportunity to modify the chemistry of hydrocarbons to improve the properties of petroleum base oils. Quantitative ¹H and ¹³C NMR data has been used to generate average structural profile for a variety of base oil samples and aromatic fractions. The average structural parameters were used to study the effect of hydroprocessing on structure and properties of paraffinic neutral base oils. In addition, the effect of severity of hydrogenation on structure and properties has been investigated on three aromatic extract fractions obtained from different degree of hydrogenation of catalytic cycle stock. A linear relationship was found between average structural parameters and properties such as viscosity index, volatility and refractive index. Thermo-oxidative stability of samples was measured using differential scanning calorimetry and thin film micro oxidation tests. Variation in oxidative stability of various samples was explained using structural parameters. The NMR data was found useful in explaining property changes as a result of hydroprocessing. The results suggest that deepest knowledge of chemical structure could help in selecting base oils to meet future product specifications.

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1. Introduction

Lubricating base oils are lubricant components that provide an oil layer between moving surfaces, and remove heat and wear particles while keeping friction and wear at minimum. To fulfill these requirements, base oils must possess certain lubricant properties. These properties are in turn dependent on the chemical composition and structures of the hydrocarbon molecules present in the base oil, which are controlled by the refining process and the degree of refining of the base stock [1,2]. A quantitative indication of the degree and severity of refining of base oils can be obtained from compositional and structural data on base oils obtained from base stocks. Synthetic base stocks such as polyalphaolefins (PAO) are expensive than petroleum base stocks, but are tailor made to

provide excellent properties. The use of catalytic hydrocracking/isodewaxing/hydrofinishing technology provides an opportunity to improve the properties of less expensive mineral base stocks [3–5]. During the hydrocracking, many chemical reactions can occur including ring-opening, cyclization and isomerization and thus results in nearly total removal of heteroatomic molecules and saturation of all but a few percent of the most thermodynamically stable aromatic species [6,7]. The base oils thus produced exhibit superior performance properties, but can cause solubility limitations with certain additives. It is therefore necessary to understand the variation in the performance properties of base oils on the basis of chemical structures present in it.

The thermo-oxidative degradation of modern lubricants is mainly responsible for poor engine performance and has been

* Corresponding authors. Department of Chemical Engineering, Pennsylvania State University, University Park, PA 16802, USA. Tel.: +1 309 681 6065; fax: +1 309 681 6340.

E-mail addresses: Brajendra.Sharma@ars.usda.gov (B.K. Sharma), Sevim.Erhan@ars.usda.gov (S.Z. Erhan).

identified as the most important limiting factor for lubricant application [8,9]. Apart from other factors such as engine design, operating conditions, etc., the composition of base oil plays an important role in the oxidation stability and other performance properties. Versatile thermal techniques such as differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), differential thermal analysis, derivative thermogravimetry, and thin film micro oxidation tests (TFMO), have been widely used to study the thermo-oxidative stability of base oils and finished lubricants [10–15]. The basic approach involves monitoring a particular property of the system with change of temperature or different times at isothermal temperature.

Mass spectrometry was reported to be a useful technique in assessing the severity of hydrocracking [16,17]. Nuclear magnetic resonance (NMR) spectroscopy has emerged as a technique with a potential for understanding carbon and hydrogen distribution of base oils in terms of their average structural parameters [18–21]. These structural parameters can be related to the bulk properties of the lubricating base oils [22–28]. NMR has also been used for monitoring the degree of refining of base oils [29,30].

In this study, base oils such as naphthenic neutral, paraffinic neutral and polyalphaolefins has been selected for physical and chemical characterization. The effect of hydrogenation on structure and properties of paraffinic neutral and naphthenic neutral has been studied. In addition, the effect of severity of hydrogenation on structure and properties has been investigated on three aromatic extract fractions obtained from different degree of hydrogenation of catalytic cycle stock. PAO sample has been included in this work to act as fully saturated reference for the base stocks evaluated. The thermo-oxidative stability of these oils has been assessed using thin film micro oxidation, pressure differential scanning calorimetry (PDSC), and thermo gravimetric analysis. Chemical structure of the base oils were obtained in terms of average structural parameters obtained using quantitative ^1H and ^{13}C NMR experiments. The data collected have been used to develop a better understanding of the various relationships between base-stock chemical structure, physical properties and oxidation performance.

2. Experimental

2.1. Samples

The details of the lubricant base oils and fractions used in this study along with physicochemical characteristics are given in Table 1. Base oil PN is a paraffinic neutral and the sample obtained after its hydrogenation is HPN. Samples NN and PAO are naphthenic neutral and polyalphaolefin base oils respectively. Sample HA1 is obtained after first hydrogenation of aromatic extract fraction of catalytic cycle stock, HA2 after second hydrogenation of same aromatic fraction and HA3 is the product of third hydrogenation of same fraction. The physicochemical properties such as viscosity at 40 and 100 °C (ASTM D445), viscosity index (ASTM D2270), refractive index at 20 °C (ASTM D1218) of these samples were measured using ASTM standard test procedures. TGA Noack volatility was obtained as per ASTM D 6375-05 method using TGA (model Q 500, TA Instruments, New Castle, DE).

Table 1 – Physico-chemical characteristics of lubricant base oils and fractions (KV is kinematic viscosity, VI is viscosity index, and RI is refractive index)

	TGA Noack volatility, (%)	KV at 40 °C, cSt	KV at 100 °C, cSt	RI at 20 °C	VI
PN	5.8	84.2	9.9	1.4809	96
HPN	6.1	79.96	9.676	1.4773	99
NN	98.8	30.53	5.045	1.4761	89
HA1	52.5	92.24	5.899	1.5819	3
HA2	57.2	64.11	5.1	1.567	6
HA3	64.7	35.27	4.16	1.5384	20
PAO	10.6	22.83	5.05	1.4574	155

2.2. NMR

Quantitative ^1H and ^{13}C NMR spectra of all the samples were recorded on a Bruker DRX 300 NMR spectrometer operating at 300.13 MHz for ^1H and 75.47 MHz for ^{13}C using a C/H dual 5 mm probe. The experiments were performed at room temperature. Chemical shifts were measured with respect to tetramethylsilane (TMS) used as an internal standard. For ^{13}C NMR experiments an inverse gated decoupling scheme was used to suppress unwanted nuclear Overhauser enhancement (NOE). A 50% (w/w) sample solution was prepared in deuterated chloroform solvent (99.8%D, Sigma Aldrich) containing ~0.1 M tris(acetylacetonato) chromium (III), $\text{Cr}(\text{acac})_3$ as relaxation agent to induce the spin-lattice relaxation time [24,27,28]. In this case, a $\pi/2$ pulse width of 8.25 μs , sweep width of 26.3 kHz, and relaxation delay of 5.0 s were employed. Typically, 16 scans for ^1H and 4 K repeated scans for ^{13}C experiments were found to be optimum for enhancing the signal-to-noise ratio for obtaining quantitative spectra. Structural parameters on these oils were computed [24,27,28] from the data obtained from ^1H and ^{13}C NMR measurements.

2.3. TFMO

TFMO test was conducted by oxidizing a small amount of oil (25 μl) spread as a thin film on an activated high carbon steel catalyst surface under a steady flow (20 cc/min) of dry air. A constant air flow ensured removal of volatile oxidation products and a steady air blanket on the thin oil film without encountering gas diffusion limitation. Oxidation was carried out inside a bottomless glass reactor at 225 °C for 60 min. The temperature was maintained at ± 1 °C with a heated aluminum slab placed on top of a hot plate (MirakTM with built-in thermocouple controller by Thermolyne Inc., Dubuque, IA). This arrangement eliminates temperature gradient across the aluminum surface and transferred heat to the catalysts placed on the slab.

After oxidation, the catalyst containing the oxidized oil sample was removed from the oxidation chamber and cooled rapidly under a steady flow of dry nitrogen gas and transferred to a desiccator for temperature equilibration. After approximately 2 h, the catalyst containing the oxidized oil was weighed to determine the volatile loss (or gain) due to oxidation and then soaked in tetrahydrofuran to dissolve the soluble portion of the oxidized oil. After dissolving the soluble portion of the oxidized oil, the catalyst with the remaining insoluble deposit was dried and weighed to determine the remaining insoluble deposit.

2.4. PDSC

The PDSC experiments were done using a DSC 2910 thermal analyzer from TA Instruments. The DSC was first temperature calibrated using the melting point of indium (156.6 °C) at a 10 °C/min program rate. Optimally 1.5–2.0 mg of sample was taken in a hermetically sealed

aluminum pan with a pinhole lid for gas interaction. Dry air was pressurized in the module at a constant pressure of 1379 kPa (200 psi) and a heating rate of 10 °C/min was used throughout the length of the experiment. The signal maximum (SM) and onset (OT) temperatures of oxidation were calculated from the exotherm in each case. OT is when rapid oxidation occurs and the rate of oxygen consumption is significantly high resulting in the formation of high molecular weight oxypolymeric compounds. SM denotes the peak max temperature of oxidation and is useful in computing various kinetic data.

3. Results and discussion

Table 1 presents the physicochemical properties of two paraffinic neutral, one naphthenic neutral, three aromatic extracts and a polyalphaolefin base oil samples. All the oils except the two paraffinic neutrals are in the low-viscosity range. The paraffinic neutrals fall into the intermediate-viscosity range. Compared to PAO and NN base oils, the aromatic extracts have higher viscosities at 40 °C, but similar viscosities at 100 °C resulting into very low viscosity indices for aromatic extracts. VI is least for aromatic extracts followed by naphthenic and paraffinic and very high for PAO. The refractive index (RI) of aromatic extracts is

higher compared to others, followed by paraffinic and naphthenic and least for PAO. These differences in VI and RI are attributed to the structures present in these samples. The VI of the samples decreases with increase in their RI. The volatility is lower for paraffinic samples including PN, HPN and PAO, while it is higher for aromatics and maximum for naphthenics. Two separate trend lines can be obtained for two compound groups, one class involving ring structures, while the other class involves straight or branched paraffins. For both compounds groups, as the viscosity increases, the volatility of the samples decreases. The volatility of compound group with ring structures is higher than the one with straight or branched paraffins.

The aromatic extract samples were generated during the processing of intermediate viscosity lubricant basestock for making high VI grade basestocks. These aromatic extracts have high viscosity and thus have use in mechanical systems operating at high temperatures and have potential for use in boundary lubrication.

A close analysis of physicochemical properties is useful in understanding the nature of base oils. Although these values are based on bulk property measurements, they provide a reasonable guideline for their further processing. It is also

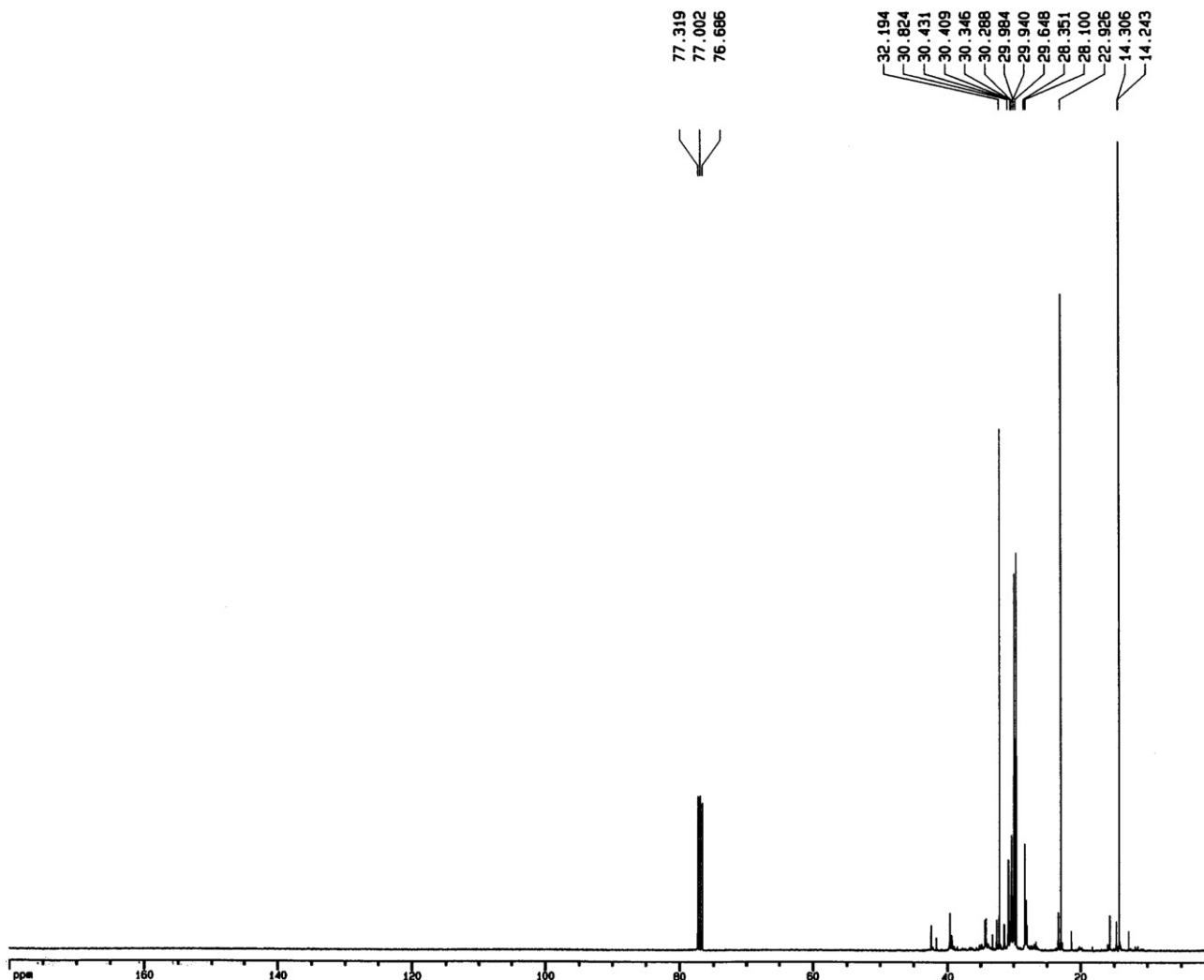


Fig. 1 – ^{13}C NMR spectrum of base oil.

interesting to note that various physical properties are interrelated in the base oils providing an ideal situation where these phenomena can be observed clearly.

3.1. Average Structural Parameters (ASPs) using NMR

Quantitative estimation of the carbon content by ^{13}C NMR was done using an inverse gated decoupling sequence and was considered quite adequate in the present situation. This has resulted in the accurate estimation of various carbon types without any assumptions on chemical shifts [31–33]. The area covered under a specific peak was translated to its relative concentration corresponding to a particular carbon type. The proton decoupled inverse gated ^{13}C NMR spectra resulted in well-separated peaks with no overlaps between adjacent peaks as shown in Fig. 1. The intense and well-defined peaks in this spectrum are due to *n*-paraffins and iso-paraffins. The assignment of peaks to specific carbon types was based on earlier studies [18,20,23,27,28,32,33]. ^{13}C NMR spectra provide important details on different types of carbon atoms present in the average structure of base oils. The carbons atoms are first divided into saturate (CS; 5–60 ppm) and aromatic (CA; 100–160 ppm) types. The CS carbon atoms are then further divided into paraffinic (CP) and naphthenic carbons (CN) using the algorithms defined in Table 2. The CP parameter is then divided into normal paraffinic (CPN) and isoparaffinic carbons (CPI). The CPN group further consists of terminal carbons on long alkyl chains (CPN_α), atoms 1 carbon away from terminal carbon

Table 3 – NMR derived average structural parameters of samples

NMR parameters	HA1	HA2	HA3	NN	PN	HPN	PAO
CA	46.4	40.1	25.0	0.0	4.5	2.4	0.6
CAH	24.1	21.6	13.6	0.0	nd	nd	nd
CAM	16.7	13.8	8.3	0.0	nd	nd	nd
CAA	5.6	4.7	3.1	0.0	nd	nd	nd
CS	53.6	59.9	75.0	100.0	95.5	97.6	99.4
CPN	19.5	22.8	7.2	16.2	41.4	37.3	58.3
CPI	24.9	22.3	16.4	28.5	38.4	29.2	41.0
CN	9.2	14.8	51.5	55.3	15.7	31.0	0.0
ACL	11.5	11.9	12.7	8.7	16.1	14.5	9.1
C/H ratio	0.651	0.625	0.571	0.500	0.512	0.506	0.502
BI	0.5	8.9	18.9	63.5	33.8	34.4	27.2

(CPN_β), 2 carbons away from terminal carbon (CPN_γ), 3 carbons away from terminal carbon (CPN_δ), 4 or more carbons removed from terminal carbon (CPN_n) as shown in Table 2. The assignment of peaks arising from naphthenic carbons is more difficult due to the large number of possible stereoisomers and the existence of strong internal strains in substituted cycloalkanes, which results in the dispersion of resonance frequencies. Using ^{13}C -NMR, naphthenic carbons are identified by broad hump in 24–60 ppm region that can be quantified by manual spline baseline correction [27]. In earlier approaches, only the hump in the region of 20–45 ppm was taken for naphthenic carbons. This excluded naphthenic carbons in the 45–60 ppm region resulting from substituted polycyclic naphthenic carbons. In this study, both the 45–60 ppm and 20–45 ppm regions are exploited. This procedure eliminates overestimation of total paraffins and underestimation of naphthenes [24,27]. In the ^{13}C NMR spectra of paraffinic base oils, very weak signals due to aromatic carbons (100–160 ppm) are observed confirming the very low aromatic content of these oils. The aromatic carbons (CA) in aromatic extracts are higher and are further divided into protonated aromatic carbons (CAH), aromatic carbons with alkyl substitution having 2 or more carbons (CAA), bridgehead or internal aromatic carbons and aromatic carbons with methyl substitution (CAM). Excellent repeatability (standard deviation of approximately 2.0 wt.%) is typically obtained in the estimation of paraffinic and naphthenic carbons from ^{13}C NMR spectra. The ^{13}C and ^1H NMR derived parameters for various samples are reported in Table 3. These parameters were then subsequently used for studying the relationship with physical and thermo-oxidative properties, and effect of hydrogenation.

The PAO mainly consists of normal and iso-paraffinic carbons only. In the base oils with considerable amount of aromatics, the naphthenic rings form the periphery of a highly condensed aromatic core, such as in HA1, HA2, and HA3.

The compositional data in Table 3 showed that the naphthenic and PAO base oils do not have any aromatic carbons, while paraffinic (PN and HPN) base oils have less than 5% CA. CPI carbons are higher in PN and PAO base oils (38–41%) followed by naphthenic and HPN (28–29%) and least in aromatics samples (16–25%). CPN carbons are highest in PAO (58%) followed by paraffinic base oils (37–41%) and minimum in aromatics and naphthenic (7–22%). For base oils like PAO, naphthenic, and paraffinic (PN and HPN), it has been shown

Table 2 – Algorithms for average structural parameters of base oils

Parameter	NMR region/peak positions
<i>Structural parameters from ^{13}C NMR data</i>	
Saturated carbons (CS)	5–60 ppm
Naphthenic carbons (CN)	Hump in region 60–24 ppm
Paraffinic carbons (CP)	CS–CN
<i>n</i> -paraffinic α carbon (CPN_α)	14.1 ppm
<i>n</i> -paraffinic β carbon (CPN_β)	22.7 ppm
<i>n</i> -paraffinic γ carbon (CPN_γ)	32.0 ppm
<i>n</i> -paraffinic δ or higher carbon (CPN_n)	29.4 & 29.9 ppm
Normal paraffins (CPN)	$\text{CPN}_\alpha + \text{CPN}_\beta + \text{CPN}_\gamma + \text{CPN}_n$
Iso paraffins (CPI)	CP–CPN
Aromatic carbons (CA)	100–160 ppm
Protonated aromatic carbons (CAH)	129.3–100 ppm
Methyl substituted and bridgehead CAs (CAM)	137.1–129.3 ppm
Alkyl substituted (excluding methyl) CAs (CAA)	160–137.1 ppm
Average chain length (ACL)	$2 \times \text{CPN} / \text{CPN}_\alpha$
C/H ratio	$(\text{CS} + \text{CA}) / (2\text{CS} + \text{CA})$
<i>Structural parameters from ^1H NMR data</i>	
CH_3 protons of alkyl chains γ or further from aromatic ring or CH_3 of saturated compounds (HS_{CH_3})	1.00–0.5 ppm
CH_2 & CH protons of alkyl chains β or further to ring and CH_3 protons β to the ring ($\text{HS}_\beta + \gamma$)	2.00–1.00 ppm
Branchiness Index (BI)	$100 * \text{HS}_{\text{CH}_3} / \text{HS}_{\beta + \gamma}$

that as the aromatic content is reduced and approached zero, oxidation stability is primarily influenced by polynaphthenic content and their relative distribution [34].

3.2. Relationship between base oil structure and physical properties

Viscosity-temperature characteristic of base oil is an important parameter for lubricant formulation, and is represented by viscosity index (VI). VI is largely dependent on the amount of CPN, CPI and to a certain extent on CN in the base oil. Therefore, high CPI and CPN percent will result in high VI [24]. The higher VI of PAO in comparison to other base oils can be explained from their carbon type distribution. The CPI and CPN content of PAO is much higher than other samples, while naphthenic carbons are absent in it. VI also provided good correlation coefficient (R^2) values with CA (0.83), CS (0.83), and C/H ratio (0.81). VI of the oils increases with an increase in CS, and decrease in CA and C/H ratio [24]. The average chain length (ACL) represents the number of carbons in *n*- and iso-paraffin chains and also as part of the side chains attached to aromatic and naphthenic rings [24,27]. It is also observed that among the paraffinic oils (PN, HPN and PAO), VI increases with decrease in average chain length. ACL also affects the kinematic viscosity at 40 °C and 100 °C. Viscosity of base oils increases with an increase in ACL. Estimation of ACL for paraffins as well as side chains attached to naphthenic and aromatic structures are useful in predicting this property. New generation base oils like PAO, PN and HPN are saturate dominant and other molecular species (poly-naphthenes, aromatics and naphthenoaromatics) do not contribute much to the physical properties. It is, therefore, important to control the ACL of saturated molecules during refining by proper selection of catalyst and reaction severity [35].

A linear relationship was found to exist between refractive index of the base oils and their aromatic ($R^2=0.98$), saturate carbons ($R^2=0.98$), and C/H ratio ($R^2=0.97$). Higher aromatic carbons and C/H ratio in base oils tend to increase the refractive index while higher saturated carbons tend to lower the refractive index (Fig. 2).

Simple linear regression of average structural parameters to VI produced a maximum R^2 value of 0.83. This indicates that VI prediction cannot be solely based on a single parameter model, and the accuracy of predicting base oil VI can be further increased by using two or more average structural parameters in multilinear regression models. Development of such models

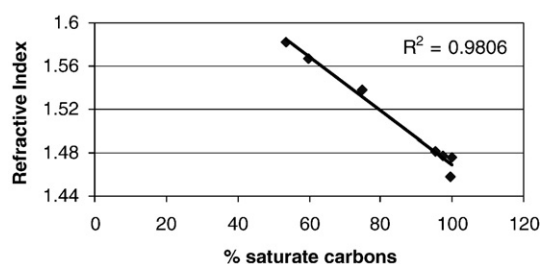


Fig. 2 – Correlation plot between refractive index (RI) and saturate carbons (CS) of base oils ($R^2=0.99$).

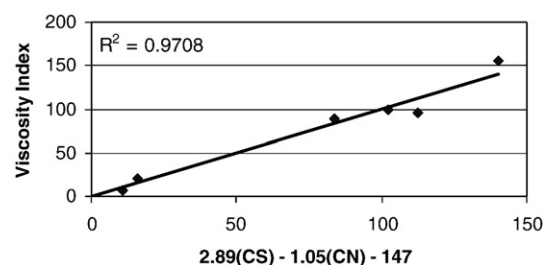


Fig. 3 – Model of viscosity index from average structural parameters using a combination of saturate (CS) and naphthenic (CN) carbons (R^2 of 0.97).

is well documented in other papers [24,26–28]. On using CA and CPN as predictors for base oil VI, the R^2 value increases to 0.97. A combination of CS and CN also results in R^2 value of 0.97 (Fig. 3).

It can thus be concluded that most of the variations in physical properties can be explained in terms of average structural parameters of base oils. These structural parameters are average representation of the relative distribution of various complex hydrocarbon structures present in base oils. As the physical properties are controlled by the relative abundance and structure of the hydrocarbons present, their detailed characterization is required for base oils with best set of properties.

3.3. Relationship between base oil structure and thermo-oxidative properties

The thermal properties of base oils can be determined using DSC by measuring the rate of heat flow evolved from or supplied to the sample as a result of exothermic or endothermic reactions [36]. The use of high pressure in DSC cells is essential to suppress the evaporation of lubricants [13]. PDSC has been shown to be an effective tool in the measurement of oxidative stability in lubricants [37–39]. PDSC is used to measure onset temperatures from the thermograms, which is a measure of oxidation stability of base oils (Table 4). The OT is the temperature at which a rapid increase in the rate of oxidation is observed and obtained by extrapolating the tangent drawn on the steepest slope of reaction exotherm to the baseline. A high OT would suggest a high oxidation stability of the oil. In general the aromatics displayed a higher range of onset oxidation

Table 4 – Oxidation stability of samples using thin film micro oxidation test at 225 °C for 1 h, and PDSC at 10 °C/min (OT is onset and SM is signal maximum temperature)

	TFMO		PDSC	
	Evaporation, %	Insoluble deposit, %	OT, °C	SM, °C
PN	69.3	21.4	194	–
HPN	72.3	23.9	198	210
NN	100.0	0.0	196	206
HA1	93.7	1.2	217	249
HA2	94.6	2.2	221	263
HA3	95.7	3.0	230	269
PAO	92.5	5.9	196	209

temperatures from 217 to 230 °C, while paraffins including normal, iso- and cyclo- displayed a lower range of onset temperatures from 194 to 198 °C. Hydrogenated aromatic extracts are more stable to oxidation than paraffins. Using the signal maxima temperatures as a measured value, the same trend is displayed. The maximum R^2 value is obtained with CPI (0.76) followed by CAH (0.72) and CAA (0.71). Relative abundance and position of branching sites influence oxidation and several other physical properties of base oils. More branchings in alkyl chains (BI) lead to lower OT or oxidation stability of base oils. Among the aromatic extracts, the higher alkyl substitution (CAA) in HA1 in conjunction with polycondensed structures explains the lower oxidation stability. Base oils having such structures are susceptible to thermal and oxidative degradation and also lead to increase in viscosity, total acid number and metal corrosion [40]. For aromatic fractions, the R^2 value for predicting OT using alkyl substituted aromatic carbons (CAA) is 0.99. Apart from average structural parameters, OT also shows good linear correlation with refractive index (0.72) and inverse linear with VI (0.75).

The R^2 value obtained for predicting oxidation stability or OT with single component is 0.76 using CPI. The predictability of OT can be further increased by using multi-components in multilinear regression models. The R^2 value increased to 0.99 with CAM and CAA, 0.93 with CPI and BI (Fig. 4), 0.90 with CPI and CN, and 0.87 with CS and CPI. One of these models can be used to predict oxidation stability of base oils more accurately.

In most applications, lubricants act as thin film, so thin film micro oxidation (TFMO) test best simulates industrial conditions where oxygen diffusion is not limiting [41]. The TFMO is a method of choice for quantitative evaluation of base oils thermal and oxidative stability, because of its simplicity, data reproducibility and a strong correlation with the time consuming rotary bomb oxidation test [15,37]. During the oxidation process, several primary oxidation products are formed. The evaporation is observed at each stage of heating as a result of fragmentation of the molecules and the other molecules undergo oxidation in presence of excess oxygen to form unstable intermediate oxy compounds that later form high molecular weight insoluble deposits. The tendency to form such deposits is the main detrimental factor in their use as high-temperature lubricants. The volatile loss obtained from TFMO tests may be used to predict the useful life of lubricants, as it provides information about the amount of

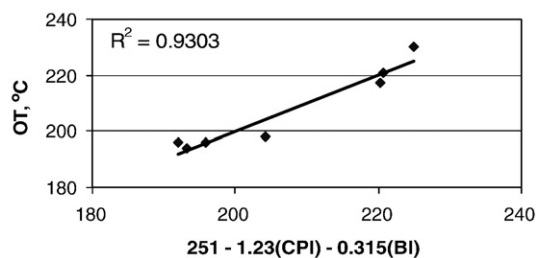


Fig. 4 – Model of onset temperature (OT) from average structural parameters using a combination of isoparaaffinic carbons (CPI) and branchiness index (BI) with correlation coefficient 0.93.

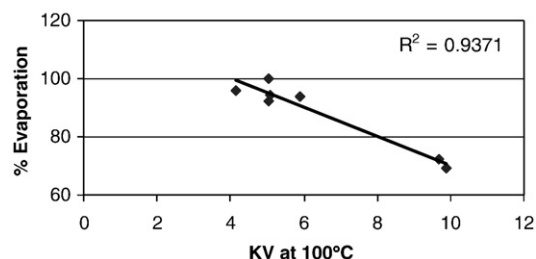


Fig. 5 – Model of percent evaporation (obtained using thin film micro oxidation test) from kinematic viscosity at 100 °C (R^2 value of 0.94).

base fluid left for lubrication, in the form of un-oxidized oil, polar oxidation products and polymerized products. In order to generate information regarding the repeatability of the TFMO test, the oxidation test at 225 °C was performed in quadruplicate for 1 h on base oil samples and standard deviation of 0.08 was obtained. The coefficient of variation is 4.5% and the % weight loss values varied within ± 0.1 of the average. This shows that the data generated in this study is accurate and reliable.

Evaporation is found to be highest for naphthenic and lowest for paraffinic. TGA results also show that overall the paraffinic neutrals have minimum volatility followed closely by PAO. The aromatics have much higher volatility than PAO, while naphthenic have the maximum volatile loss on heating. This is also supported from the low viscosity of naphthenic neutral and aromatics at 40 and 100 °C and other study [1]. The oils with low viscosity tend to form relatively less deposit during oxidation. In both compound groups (ring and other paraffins including normal and iso-paraffins), evaporation, which is associated with oxidation processes, is found to increase with an increase in VI of the oil, similar to TGA Noack volatility. Except paraffinic neutrals (PN and HPN), all other samples are stable to deposit formation tendency at 225 °C. The insoluble deposit and volatile loss obtained from TFMO produced weak correlations with base oil structural parameters except average chain length (R^2 of 0.72). Higher ACL of average base oil structure leads to lower evaporation. This may be explained on the basis of increased viscosity due to longer alkyl chains. Kinematic viscosity at 100 °C was found to be a good predictor for % evaporation with R^2 value of 0.94 (Fig. 5) and % deposit (R^2 of 0.89). An increase in viscosity at 100 °C shows a decrease in the evaporation loss during oxidation of base oil. The oils with lower viscosity (at 100 °C) tend to form relatively less deposit during the oxidation. The TGA Noack volatility provides an R^2 value of 0.65 for % evaporation and 0.64 for % insoluble deposits. Higher TGA Noack volatility thus results in higher evaporation loss and lower insoluble deposits during oxidation of base oils.

The TFMO thermo-oxidative study correlates more readily with various high temperature bearing tests. Oxidation in the TFMO test occurs on a metal surface in an open atmosphere where evaporation can occur. Therefore, test results can be used as a lubricant development and specification tool for applications in specific operating conditions and component metallurgy.

3.4. Effect of hydrogenation on structure and properties

Hydrogenation in the form of hydrocracking technology provides an opportunity to modify the chemistry of hydrocarbons for improving the performance properties of mineral base oils. No significant difference was found in the ^1H NMR spectra of paraffinic (PN) and hydrogenated paraffinic neutral (HPN) except for the branchiness index. The BI value is higher for the hydrogenated fractions compared to normal samples. It also increases with the severity of hydrogenation. The data from ^{13}C NMR spectra shows a decrease in aromatic carbons resulting in an increase of saturate carbons in base oil average structure on increasing severity of hydrogenation. The normal and iso-paraffinic carbons (CPN and CPI) decrease, while naphthenic carbons increase on hydrogenation and its severity. The C/H ratio also decreases as a result of increasing severity of hydrogenation. The average chain length of paraffinic base oils decreases with hydrogenation, while it increases in case of aromatic extracts. During hydrogenation, different aromatic carbons such as CAH, CAM and CAA also decreases in same fashion as total aromatic carbons for aromatic fractions. These differences are visible in the average structures of these oils.

The kinematic viscosity (at 40 and 100 °C) and refractive index for aromatics decreases with severity of hydrogenation. The viscosity and refractive index of paraffinic neutral also decreases on hydrogenation. This decrease in viscosity and refractive index on hydrogenation is due to decrease in CA and CPI carbons and increase in CS and CN carbons of samples. As mentioned earlier that refractive index has a direct correlation to CA and inverse correlation to CS. On hydrogenation the VI of oil samples also increases. A decrease in average chain length (ACL) of paraffinic neutral on hydrogenation causes the VI of base oils to increase. Other structural parameters that are important in controlling VI are aromatic and saturate carbons. Aromatic carbons decrease, while saturate carbons increase and thus leading to an increase in VI of base oils on hydrogenation.

From the oxidation studies using TFMO and TGA, it was found that oils on hydrogenation show high volatile loss and increases with severity of hydrogenation. The deposit forming tendencies also increase slightly with severity of hydrogenation. The onset temperature obtained for oils using PDSC increases on hydrogenating the oil and shows an increasing pattern with severity of hydrogenation. This increase in oxidation stability on hydrogenation can be explained using isoparaffinic and naphthenic carbons. Hydrogenation results in decrease of CPI and increase of CN. CPI carbons are more susceptible to oxidation, while CN carbons are more resistant to oxidation compared to aromatic carbons. Therefore, lower CPI and higher CN results in base oils with improved oxidation stability.

The NMR data was found useful in assessing the structure-property relationships and the effect of hydrogenation on thermal and physical properties of base oils. The use of multiple linear regression formulas to predict physical properties has the inherent confusion that the sign of the predictors does not necessarily fit expectation or intuition. It should be noted that these models are most useful for predicting bulk properties, and not necessarily for

identifying the underlying chemistry responsible for these properties.

4. Conclusions

In mineral base oils, physical properties, thermo-oxidative behavior and molecular structure are intimately related. Depending on the end application of finished lubricant, it is possible to regulate the thermo-oxidative and physical behavior by controlling the relative distribution of hydrocarbon molecules in these oils, such as:

- Higher CPI and CPN content leads to higher VI of PAO.
- A decrease in average chain length among the paraffinic oils increases the VI.
- An increase in ACL increases the viscosity of base oils.
- Higher aromatic carbons and C/H ratio increases the refractive index of base oils.
- More branching in alkyl chains, lead to lower oxidation stability of base oils.
- Naphthenic base oils have higher volatility than aromatics, while paraffinic ones have lower than PAO.
- Higher ACL of average base oil structure leads to lower evaporation.

It can be concluded from the above discussion that the physical properties are not solely governed by a single structural parameter. Several structures influence a particular property to varying extents. The structure-property correlations shown here can be used as a guideline to establish such correlation models by including a large number of samples. The structural parameters can be used to track molecular composition in various extraction sequences and lubricant refining such as hydrogenation, such as:

- BI value and CN increases, while CPN decreases on hydrogenation and its severity.
- ACL of paraffinic base oils decreases with hydrogenation, while it increases in aromatic extracts.
- Viscosity and refractive index decreases with severity of hydrogenation.
- CA decrease and CS increase lead to an increase in VI of base oils on hydrogenation.
- Volatile loss increases with severity of hydrogenation.
- OT increases on hydrogenation and its severity.

The study thus shows that various process parameters and severity of operation for lubricant refining can be optimized in terms of structural data to obtain base oils with improved performance properties.

5. Disclaimer

Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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